

comes within the spirit and scope of the following claims should be considered part of the present invention.

What is claimed as new and desired to be protected by Letters Patent of the United States is:

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1. A method for removing dry etch residues from a semiconductor substrate comprising the steps of:

exposing a semiconductor substrate having dry etch residues thereon to a  
5 conditioning solution, wherein the conditioning solution comprises a fluorine source, a complementary acid, and a non-aqueous solvent.

2. The method of claim 1, wherein the fluorine source is HF.

3. The method of claim 1, wherein the fluorine source is  $\text{NH}_4\text{F}$ .

4. The method of claim 1, wherein the complementary acid is  $\text{H}_3\text{PO}_4$ .

10 5. The method of claim 1, wherein the complementary acid is a phosphate salt.

6. The method of claim 1, wherein the complementary acid is HCl.

7. The method of claim 1, wherein the complementary acid is a pH suppressant.

15 8. The method of claim 1, wherein the non-aqueous solvent is a polyhydric alcohol.

9. The method of claim 1, wherein the non-aqueous solvent is propylene glycol.

10. The method of claim 1, wherein the non-aqueous solvent is ethylene glycol.

11. The method of claim 1, wherein the non-aqueous solvent is tetrahydrofuran.

12. The method of claim 1, wherein the non-aqueous solvent is dimethylsulfoxide.

13. The method of claim 1, wherein the non-aqueous solvent is propylene carbonate.

14. The method of claim 1, wherein the non-aqueous solvent is isopropyl alcohol.

15. The method of claim 1, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, and the complementary acid is  $\text{H}_3\text{PO}_4$ .

16. The method of claim 15, wherein the HF, propylene glycol, and  $\text{H}_3\text{PO}_4$  are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 95 : 1 – 15.

17. The method of claim 15, wherein the HF, propylene glycol, and  $\text{H}_3\text{PO}_4$  are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 89 – 94 : 6 – 7.

18. The method of claim 15, wherein the HF, propylene glycol, and  $\text{H}_3\text{PO}_4$  are present in the conditioning solution in the approximate proportion of 0.27 : 91.5 : 6.5.

19. The method of claim 1, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, and the complementary acid is HCl.

20. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0.

21. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 93 – 98 : 0.005 – 0.009.

22. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.27 : 97.5 : 0.006.

23. The method of claim 1, wherein the conditioning solution further comprises a surface passivation agent.

24. The method of claim 23, wherein the surface passivation agent is a carboxylic acid.

5 25. The method of claim 23, wherein the surface passivation agent is citric acid.

26. The method of claim 23, wherein the surface passivation agent is acetic acid.

27. The method of claim 23, wherein the surface passivation agent is EDTA.

10 28. The method of claim 23, wherein the surface passivation agent is an organic acid.

29. The method of claim 23, wherein the surface passivation agent is ascorbic acid.

15 30. The method of claim 23, wherein the surface passivation agent is a chelant.

31. The method of claim 23, wherein the surface passivation agent is a reducing agent.

32. The method of claim 23, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.

33. The method of claim 32, wherein the HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

34. The method of claim 32, wherein the HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.09 – 0.5.

35. The method of claim 32, wherein the HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion of 0.27 : 91.5 : 6.5 : 0.25.

36. The method of claim 23, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

37. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

38. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.25 - 0.3 : 93 - 98 : 0.005 - 0.009 : 0.09 - 0.5.

39. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.27 : 97.5 : 0.006 : 0.25.

40. The method of claim 1, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

41. The method of claim 1, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

42. The method of claim 1, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

43. The method of claim 1, wherein said exposure step further comprises immersing the substrate in the conditioning solution.

44. The method of claim 1, wherein said exposure step further comprises dispensing the conditioning solution onto the substrate.

45. The method of claim 1, wherein said exposure step is performed for a time sufficient to remove substantially all dry etch residues from the substrate.

46. The method of claim 1, wherein said exposure step is performed for approximately 10 seconds or longer.

5 47. The method of claim 1, wherein said exposure step is performed for approximately 60 seconds or longer.

48. The method of claim 1, further comprising rinsing the substrate after said exposure step.

49. The method of claim 48, wherein said rinsing step comprises exposing the  
10 substrate to deionized water.

50. The method of claim 48, wherein said rinsing step comprises exposing the substrate to an aqueous acid solution.

51. The method of claim 50, wherein the aqueous acid solution is a solution of a carboxylic acid.

15 52. The method of claim 50, wherein the aqueous acid solution is a solution of citric acid.



53. The method of claim 50, wherein the aqueous acid solution is a solution of EDTA.

54. The method of claim 50, wherein the aqueous acid solution is a solution of acetic acid.

5 55. The method of claim 50, wherein the aqueous acid solution is a solution of an organic acid.

56. The method of claim 50, wherein the aqueous acid solution is a solution of ascorbic acid.

10 57. The method of claim 50, wherein the aqueous acid solution is a solution of carbonic acid.

58. The method of claim 50, wherein the aqueous acid solution is buffered to a pH between approximately 4.0 and approximately 8.0.

59. The method of claim 48, wherein said rinsing step comprises exposing the substrate to an organic solvent.

15 60. The method of claim 59, wherein the organic solvent is propylene glycol.

61. The method of claim 48, wherein said rinsing step comprises exposing the substrate to a solution containing an anti-etch agent.

62. The method of claim 61, wherein the anti-etch agent is ammonium lactate.

63. The method of claim 61, wherein the anti-etch agent is boric acid.

64. The method of claim 48, wherein said rinsing step further comprises  
5 immersing the substrate in a rinse bath.

65. The method of claim 64, wherein said rinsing step further comprises  
agitating the rinse bath.

66. The method of claim 65, wherein the rinse bath is agitated with  
megasonic energy.

10 67. The method of claim 65, wherein the rinse bath is agitated by bubbling a  
gas through the rinse bath.

68. The method of claim 67, wherein CO<sub>2</sub> is bubbled through the rinse bath.

69. The method of claim 67, wherein N<sub>2</sub> is bubbled through the rinse bath.

70. The method of claim 48, further comprising pre-rinsing the substrate with  
15 a non-aqueous solvent subsequent to said exposing step but prior to said rinsing step.

71. The method of claim 70, wherein the non-aqueous solvent is a polyhydric alcohol.

72. The method of claim 70, wherein the non-aqueous solvent is propylene glycol.

5 73. The method of claim 70, wherein the non-aqueous solvent is the same non-aqueous solvent used in the conditioning solution.

74. A method for removing dry etch residues from a semiconductor substrate comprising the steps of:

10 treating a semiconductor substrate having dry etch residues thereon with a conditioning solution, wherein the conditioning solution comprises a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent.

75. The method of claim 74, wherein the fluorine source is HF.

76. The method of claim 74, wherein the fluorine source is  $\text{NH}_4\text{F}$ .

15 77. The method of claim 74, wherein the non-aqueous solvent is a polyhydric alcohol.

78. The method of claim 74, wherein the non-aqueous solvent is propylene glycol.

79. The method of claim 74, wherein the non-aqueous solvent is ethylene glycol.

80. The method of claim 74, wherein the non-aqueous solvent is tetrahydrofuran.

5 81. The method of claim 74, wherein the non-aqueous solvent is dimethylsulfoxide.

82. The method of claim 74, wherein the non-aqueous solvent is propylene carbonate.

83. The method of claim 74, wherein the non-aqueous solvent is isopropyl  
10 alcohol.

84. The method of claim 74, wherein the complementary acid is  $\text{H}_3\text{PO}_4$ .

85. The method of claim 74, wherein the complementary acid is a phosphate salt.

86. The method of claim 74, wherein the complementary acid is  $\text{HCl}$ .

15 87. The method of claim 74, wherein the complementary acid is a pH suppressant.

88. The method of claim 74, wherein the surface passivation agent is a carboxylic acid.

89. The method of claim 74, wherein the surface passivation agent is citric acid.

5 90. The method of claim 74, wherein the surface passivation agent is acetic acid.

91. The method of claim 74, wherein the surface passivation agent is EDTA.

92. The method of claim 74, wherein the surface passivation agent is an organic acid.

10 93. The method of claim 74, wherein the surface passivation agent is ascorbic acid.

94. The method of claim 74, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

15 95. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

96. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.09 – 0.5.

97. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

98. The method of claim 74, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.

99. The method of claim 98, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

100. The method of claim 98, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

101. The method of claim 98, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

102. The method of claim 74, wherein the conditioning solution is a solution composed of approximately 0.01 to approximately 5.0 percent of the fluorine source, approximately 80 to approximately 90 percent non-aqueous solvent, approximately 1 percent to approximately 15 percent of the complementary acid, and approximately  
5 0.001 to approximately 1.0 percent of the surface passivation agent.

103. The method of claim 74, wherein the conditioning solution is a solution composed of approximately 0.01 to approximately 5.0 percent of the fluorine source, approximately 80 to approximately 95 percent non-aqueous solvent, approximately 0.003 percent to approximately 1.0 percent of the complementary acid, and  
10 approximately 0.001 to approximately 1.0 percent of the surface passivation agent.

104. The method of claim 74, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

105. The method of claim 74, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

15 106. The method of claim 74, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

107. The method of claim 74, wherein said exposure step is performed for a time sufficient to substantially remove all dry etch residues from the substrate.

108. The method of claim 74, wherein said exposure step is performed for approximately 60 seconds or longer.

109. The method of claim 74, further comprising rinsing the substrate after said exposure step.

5 110. A method for cleaning a wafer after a dry etch process comprising the steps of:

treating a wafer having at least one of organometallic and organosilicate residues on exposed surfaces of the wafer with a conditioning solution composed of a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent  
10 until the residues are removed from the wafer.

~~111. The method of claim 110, further comprising rinsing the substrate after said treating step.~~

112. The method of claim 110, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface  
15 passivation agent is citric acid.

113. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.



114. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.009 – 0.5.

115. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

116. The method of claim 110, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.

117. The method of claim 116, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

118. The method of claim 116, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

119. The method of claim 116, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

120. The method of claim 110, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

121. The method of claim 110, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

5 122. The method of claim 110, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

123. The method of claim 110, wherein said exposure step is performed for approximately 60 seconds or longer.

10 124. A method for processing a substrate with patterned photoresist on the substrate surface comprising the steps of:

providing a substrate with patterned photoresist on a surface of the substrate;

performing a dry etch process on the substrate;

removing any remaining photoresist from the surface of the substrate; and

15 exposing the substrate to a conditioning solution of a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent.

125. The method of claim 124, further comprising rinsing the substrate after said exposure step.

126. The method of claim 124, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

127. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

128. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.009 – 0.5.

129. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

130. The method of claim 124, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.

131. The method of claim 130, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

132. The method of claim 130, where HF, propylene glycol,  $H_3PO_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

133. The method of claim 130, where HF, propylene glycol,  $H_3PO_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

134. The method of claim 124, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

135. The method of claim 124, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

136. The method of claim 124, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

137. The method of claim 124, wherein said exposure step is performed for approximately 60 seconds or longer.

138. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, HCl, and citric acid in the approximate ratio 0.01-5.0 : 80-95 : 0.003 - 1.0 : 0.001-1.0.

139. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol,  $H_3PO_4$ , and citric acid in the approximate ratio 0.01-5.0 : 80-90 : 1-15 : 0.001-1.0.

140. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, HCl, and citric acid in the ratio 0.25 - 0.3 : 90-98 : 0.005 - 0.009 : 0.009-0.5; and rinsing the wafer.

141. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol,  $H_3PO_4$ , and citric acid in the ratio 0.25 - 0.3 : 90-94 : 6-7 : 0.009-0.5; and

rinsing the wafer.

142. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process, said solution comprising:

hydrofluoric acid;

phosphoric acid;

propylene glycol; and

citric acid.

143. The solution of claim 142, wherein said solution consists essentially of hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid.

144. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.01 – 5.0 : 1 – 15 : 80 – 90 : 0.001 – 1.0.

145. The solution of claim 144, wherein said solution comprises approximately 0.01 to approximately 5.0 percent hydrofluoric acid, approximately 1 to approximately 15 percent phosphoric acid, approximately 80 to approximately 95 percent propylene glycol, and approximately 0.001 to approximately 1.0 percent citric acid.

146. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.25 – 0.3 : 6 – 7 : 90 – 94 : 0.009 – 0.5.

147. The solution of claim 146, wherein said solution comprises approximately 0.25 to approximately 0.3 percent hydrofluoric acid, approximately 6 to approximately 7 percent phosphoric acid, approximately 90 to approximately 94 percent propylene glycol, and approximately 0.009 to approximately 0.5 percent citric acid.

148. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.27 : 6.5 : 91.5 : 0.25.

149. The solution of claim 148, wherein said solution comprises approximately 0.27 percent hydrofluoric acid, approximately 6.5 percent phosphoric acid, approximately 91.5 percent propylene glycol, and approximately 0.25 percent citric acid.

150. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process, said solution comprising:

hydrofluoric acid;

hydrochloric acid;

propylene glycol; and

citric acid.

151. The solution of claim 150, wherein said solution consists essentially of hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid.

152. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.01 – 5.0 : 0.003 – 1.0 : 80 – 99 : 0.001 – 1.0.

153. The solution of claim 152, wherein said solution comprises approximately 0.01 to approximately 5.0 percent hydrofluoric acid, approximately 0.003 to approximately 1.0 percent hydrochloric acid, approximately 80 to approximately 99 percent propylene glycol, and approximately 0.001 to approximately 1.0 percent citric acid.

154. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.25 – 0.3 : 0.005 – 0.009 : 90 – 98 : 0.009 – 0.5.

155. The solution of claim 154, wherein said solution comprises approximately 0.25 to approximately 0.3 percent hydrofluoric acid, approximately 6 to approximately 7 percent hydrochloric acid, approximately 90 to approximately 98 percent propylene glycol, and approximately 0.009 to approximately 0.5 percent citric acid.

156. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.27 : 0.006 : 97.5 : 0.25.



157. The solution of claim 156, wherein said solution comprises approximately 0.27 percent hydrofluoric acid, approximately ~~0.006~~ percent hydrochloric acid, approximately 97.5 percent propylene glycol, and approximately 0.25 percent citric acid.

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158. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process consisting essentially of a fluorine source, a complementary acid, and a non-aqueous solvent.

159. The solution of claim 158, wherein the fluorine source is hydrofluoric acid, the complementary acid is phosphoric acid, and the non-aqueous solvent is propylene glycol.

160. The solution of claim 158, wherein the fluorine source is hydrofluoric acid, the complementary acid is hydrochloric acid, and the non-aqueous solvent is propylene glycol.

161. The solution of claim 158, wherein said solution further includes a surface passivation agent.

162. The solution of claim 161, wherein the fluorine source is hydrofluoric acid, the complementary acid is phosphoric acid, the non-aqueous solvent is propylene glycol, and the surface passivation agent is citric acid.

163. The solution of claim 161, wherein the fluorine source is hydrofluoric acid, the complementary acid is hydrochloric acid, the non-aqueous solvent is propylene glycol, and the surface passivation agent is citric acid.